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Advanced Fast Curing Adhesives for Adverse Conditions

by Daniel De Bonis and John La Scala

ARL-RP-183

July 2007

A reprint from the *Proceedings of the SAMPE 2007 Conference*,
Baltimore, MD, 3–7 June 2007.

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Army Research Laboratory

Aberdeen Proving Ground, MD 21005-5069

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ADVANCED FAST CURING ADHESIVES FOR ADVERSE CONDITIONS

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ABSTRACT

Numerous adhesives are available which provide fast, strong and durable bonding on a variety of substrates. There are however, no current adhesives which meet all these criteria when used in wet or underwater applications. Existing adhesive technology falls short of current military field requirements which often require adhesive applications be made successfully in seconds, not minutes, in cold wet environments. Research is being carried out to develop faster, low temperature curing, aquatic capable adhesives with properties equal to existing dry application formulations. A large variety of commercial adhesive formulations were characterized to determine their applicability for potential modification and use. Additives and modifiers were developed to create adhesives that quickly form strong bonds between water saturated surfaces and cure sufficiently in the presence of water. The approach to modification includes novel experimentation as well as integration of traditional adhesive chemistry in non-traditional ways.

KEY WORDS: Adhesives/Adhesive Bonding, Fast Curing, Applications – Marine

1. INTRODUCTION

Current adhesives generally perform very poorly when bonding substrates in wet or aquatic environments, especially at cold temperatures. Currently designed “waterproof” bonding adhesives generally do not bond quickly or strongly enough for rapid repair use (1). Other adhesives cure quickly but have dramatically reduced adhesion when used under wet conditions.

There are three broad classes of adhesives, including tacky substances, such as tapes, light curable adhesives, and thermally curable adhesives (2). Tape adhesives never provide weld-strength bonds and often have low tackiness when used underwater. Ultraviolet and visible light curable adhesives cure very quickly, but are not popular for field operations, especially in underwater scenarios, because the required UV/visible light source adds to the current burden soldiers need to transport. Yet, a recent invention allows the use of chemiluminescent glow sticks instead of electric light sources to cure adhesives underwater (3). However, radiation curable adhesives generally have lower adhesion, and the light does not penetrate the adhesives

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to great depths (4). This leaves only a thin strip of adhesive cured at the water interface with poor adhesion strength. Thermally cured adhesives use ambient thermal energy to induce polymerization, and the exothermic heat of reaction produced during polymerization accelerates and sustains the reaction, which proceeds via a variety of mechanisms (2). Few thermally cured adhesives result in rapid, high strength adhesion, and even fewer function in high moisture environments. Moisture reduces adhesion and the very high specific heat of water and the low water temperatures reduces exothermic cure acceleration for underwater adhesives. As a result, underwater adhesives either cure poorly or require long cure times of a day or more to obtain sufficient adhesive properties (2).

Cyanoacrylates, such as 3M CA-40 anionically polymerize in the presence of moisture. In ambient environments with ~50% humidity, cyanoacrylates can react to nearly complete cure within minutes (5). These adhesives can be used on a wide variety of substrates, but these types of adhesives are never used in wet environments and actually cure too fast and have poor properties when cured at very high humidity because too many radicals are generated, resulting in very low polymer connectivity and molecular weight.

Certain epoxy resin systems, such as National Maintenance Products NMP 3730, are formulated to set within minutes and reach near complete cure within a few hours even underwater (6). However, even this cure time is too slow for many Army applications. These epoxy adhesives are two part formulations that cure via epoxy-amine chemistry. Like cyanoacrylates, fast-cure epoxies tend to be brittle and have low peel strength. Modified formulations can have improved toughness and peel strength, but have lower thermal properties and considerably slower cure. With the exception of a small minority of epoxies, wet surfaces, high humidity, and certainly aqueous environments severely increase epoxy gel time and detrimentally affect adhesion strength.

The Army's current set of battle damage repair adhesives include Belzona 2311 elastomer, Belzona 1221 super metal, and Belzona metal plug, which are very fast curing adhesives that require only a few minutes to form high strength bonds (7). Belzona 2311 is a fast-cure polyurethane adhesive. Belzona 1221 and metal plug are epoxy-amine polymers with an added isocyanate component, which quickly reacts with amines and generates heat to speed up the epoxy-amine reaction. However, none of these adhesives can be used in high humidity environments, much less wet and marine environments (7). Therefore, there exists a need for a high performance fast-curing adhesive for field repair in humid and wet environments

Numerous existing adhesive technologies were tested to determine their bonding abilities under various conditions. Adhesive classes tested included emergency repair epoxies, underwater epoxies, marine mastic epoxies, moisture curing diphenylmethane diisocyanate (MDI), and cyanoacrylates. Each adhesive class utilized a different reaction mechanism in which it cured and formed adhesive bonds. These differences were studied and used to develop hybrid adhesives.

Properties such as cure rate, water tolerance, and bond strength were beneficially modified. Modification reduced curing time over the base adhesive while increasing dry and wet adhesive bond strength.

As cure time was proportional to temperature, the cure rate could in theory be increased by incorporation additives that produce heat when in contact with water. Additional research was performed to find ways to introduce these additives to increase cure rate while maintaining ultimate adhesive properties.

2. MATERIALS CONSIDERATION

2.1 Commercially Available Adhesives Commercially available adhesives were tested to establish their baseline properties. From each adhesive class, superior examples were selected. Products were chosen that exhibited fast curing, high strength, and low odor. Environmentally preferable products were selected when ever possible.

Belzona 1221 Super E Metal modified epoxide polymer based system was chosen as the high speed emergency repair epoxy material. This advanced low odor, high speed, high adhesion epoxy was produced by Belzona Inc. of Miami Florida. The base component is a dark gray paste with a density of 2.20-2.40 g/cm³ while the white colored solidifier component has a density of 1.10-1.30 g/cm³ (8). The mixing ratio was 2:1 by weight (base: solidifier) or 1:1 by volume (8, 9).

The underwater epoxy chosen for testing was Mr. Sticky's Underwater Glue (MSUWG) produced by AAI, of Fair Oaks, FL. This epoxy is formulated to adhere difficult to bond substrates, such as PVC, even under water (1). The epoxy came in a metered dual portioned applicator with resin and hardener in separate compartments. The left compartment contained the yellow colored curing hardener. This was comprised of triethanolamine (TETA), triethylenetetramine, aminoethylpiperazine, TETA reaction products with propylene oxide, dinonylphenol, and piperazine. The right compartment contained the white colored epoxy resin which was a mixture of crystalline silica, bisphenol A diglycidyl ether resin, butylated bisphenol A epoxy resin, and dinonylphenol (10).

Marine use A-788 Splash Zone epoxy-polyamide mastic from Z Spar, Los Angeles, CA was used for testing (11). The compound was a two part, non-volatile paste system used primarily to repair and protect exposed surfaces that are in direct contact with salt and fresh water. The benefit of this compound was its ability to be mixed and cure entirely underwater. As supplied, each of the two components was contained in 946 mL metal crimp topped containers.

Gorilla Glue was chosen as a moisture curing adhesive. The product is made in Denmark and distributed by The Gorilla Glue Company of Cincinnati, OH. It is based on a moisture sensitive formulation which includes a urethane pre-polymer hexylmethane diisocyanate and diphenylmethane-4, 4 diisocyanate (MDI) (12).

The low viscosity ethyl cyanoacrylate Scotch-Weld CA40 was obtained from 3M of St. Paul, MN (13). Cyanoacrylates are the main ingredient of super glues, which are known for fast curing in ambient conditions, but are typically not used in wet environments.

Epon 828 epoxy resin was provided by Miller-Stephenson Chemical Company, Inc. of Danbury, CT. The epoxy is an undiluted clear liquid with an epoxide equivalent weight of 185-192 g/eq, viscosity at 25° C 110-150 P and a density of 1.16 g/mL (14).

2.2 Methacrylation Catalyst Aerojet Fine Chemicals of Rancho Cordova, CA was the supplier for the AMC-2 catalyst utilized for the methacrylation of epoxies during experimentation. The catalyst is composed of 50% phthalate esters and 50% trivalent organic chromium complexes (15).

2.3 Aluminum Lap Plates Prefabricated 2024 T3 aluminum lap plates were utilized for single lap shear testing. The plates were fabricated with alignment guide holes which fit into a pegged base plate and provided a 12.7+- 0.3 mm overlap. The specimens were designed to meet the requirements of ASTM standard D 3165-95 to include ASTM B 209 "Specifications for Aluminum and Aluminum Alloy Sheet and Plate".

2.4 Methacrylic Acid Methacrylic acid was supplied in a 3 Kg amber bottle by Alfa Aesar Inc. of Ward Hill, MA. The acid had a density of 1.02 and a F.W. of 86.09.

2.5 Amine Curing Agent Amicure PACM curing agent was utilized to cure epoxy resins. The 4,4- methylenebiscyclohexanamine agent was supplied by Air Products of Allentown, PA. PACM has an amine hydrogen equivalent weight of 52.5.

2.6 Silane Coupling Agent Alfa Aesar of Ward Hill, MA supplied the γ -glycidoxypropyltrimethoxysilane (GPS- Figure 1) which was at 96% concentration. This acidic compound was used during lap specimen surface preparation.

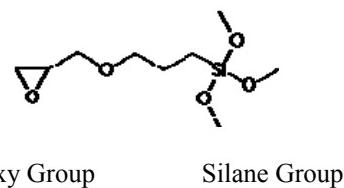


Figure 1: The structural formula of GPS showing both the epoxide and silane functional groups.

2.7 Abrasive Grit During surface preparation, the aluminum specimens were abrasive blasted using 180 grit aluminum oxide powder supplied by Treibacher Schleifmittel of Niagara Falls, NY.

2.8 MRE Heater U.S. military grade US1991 OPM64 meal ready to eat (MRE) heater packets were obtained from Zesto Therm Inc. of Cincinnati, OH. Packages utilized a patented blend of metals and salts to produce heat through super corrosion when mixed with water.

2.9 Trigonox 239A Akzo Nobel of Chicago, IL provided the Trigonox 239A. This free radical initiator is typically used to cure vinyl ester resins. This version of Trigonox contains 45% cumen hydroperoxide and is designed to produce low porosity resins (16).

2.10 Cobalt Napthenate The cobalt napthenate accelerator (CoNap) was produced by Sigma Aldrich of St. Louis MO. This accelerator breaks cumen hydroperoxide down into radicals at room temperature to cure vinyl ester resins and unsaturated polyesters.

3. EXPERIMENTAL

3.1 Methacrylated Epoxy Preparation Epon 828 is a difunctional bisphenol A epichlorohydrin derived epoxy resin. In this work, Epon 828 was partially methacrylated utilizing AMC-2 catalyst and methacrylic acid (MAA). A 2:1 molecular ratio of Epon 828 (MW 386.2 g/mol) to methacrylic acid (MW 87 g/mol) was prepared to create a 100 g sample of partially methacrylated epoxy (PME) as shown in figure 2. The two components were mixed and heated in a tri-ported, 250 mL round bottom glass vessel. The vessel was reacted at a controlled 80° C until the acid number was less than 15. This took approximately 1.5 hours to accomplish. Stoichiometric calculations indicated that the end product should be predominantly molecules with an epoxide functional group on one end and a methacrylate end group on the other.

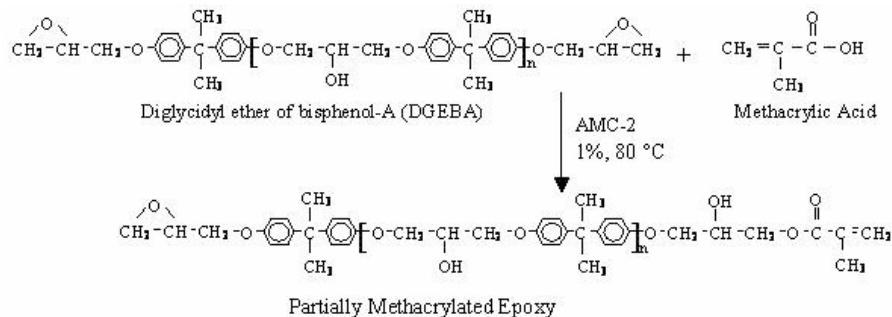


Figure 2: The reaction of methacrylic acid and DGEBA (Epon 828) to form a partially methacrylated epoxy.

3.2 Methacrylated Epoxy Characterization

3.2.1 Acid Number Acid number readings were taken using testing methods provided by ASTM D1980-87. This utilized the titration of 0.5N sodium hydroxide into 1 g sample of the sample dissolved in 5 g of acetone. Prior to titration, the dissolved sample had approximately 4 drops of phenolphthalein indicator (0.5 wt% phenolphthalein in 50% ethanol) added. Sodium hydroxide was then titrated into the magnetically stirred sample until the indicator turned pink for 30 seconds. Pink lasting for 30 seconds or more indicated the neutralization point had been reached. The amount of sodium hydroxide was recorded and acid number calculated. The acid number of 15 was used as a benchmark to discontinue heating the sample. This number corresponded to approximately 3% free acid. The final acid number for the sample was 1.8 indicating near complete acid utilization.

3.2.2 Fourier Transform Infrared Spectroscopy A Thermo Nicolet Nexus 670 FTIR unit was used in absorbance mode to determine the presence of epoxide and methacrylate functional groups in the partially methacrylated epoxy. The unit was set to scan 16 scans per spectrum at a

4 cm^{-1} resolution in the 4000-300 spectrum range. Samples of the partially methacrylated epoxy were run against both Epon 828 and methacrylic acid for comparison. The partially methacrylated epoxy exhibited both peaks for epoxy (917 cm^{-1}) and methacrylate (942 cm^{-1}) (17). This indicated that the partial methacrylation of Epon 828 was successful.

3.3 Commercial Adhesive Formulation Modification

3.3.1 Belzona 1221 GG Modified Solidifier Commercially available Belzona 1221 Super E Metal is a two component epoxy repair system. The base component contained the amine curing agent tetrapropoxylated-ethylenediamine and N,N'- dialkylamino-diphenylmethane (9). N,N'- dialkylamino-diphenylmethane is an aromatic secondary diamine chain extender for polyurethanes and is used as a secondary curative in thermosetting polyurethane materials for golf ball covers (18). The solidifier is comprised of DGEBA-epoxy resin, Hexamethylene diisocyanate (HDI) and a homopolymer of HDI (majority by wt %). HDI is a polymerizing agent for urethanes (19). This solidifier was modified by the addition of Gorilla Glue in an effort to increase the moisture curing properties.

The Gorilla glue's urethane pre-polymer, and polymeric MDI (a mixture of monomeric diphenylmethane-4,4 diisocyanate (MDI), isomers and homopolymer) (12) did not cure when mixed with the existing Belzona solidifier components. This allowed the moisture reactive components of the gorilla glue to be incorporated into the Belzona 1221 epoxy system. Two formulations were created, one with 30 wt% Gorilla glue incorporated into the solidifier and the other with 70 wt%. Both formulations yielded quality epoxy results when mixed with the base in the recommended base to solidifier ratios. In both cases, the cure reaction was much faster than the standard Belzona 1221 reaction. Based on the disclosed components of Belzona 1221 (9) and Gorilla Glue (12), the tetrapropoxylated-ethylenediamine/N,N'-dialkylamino-diphenylmethane react with the MDI of the Gorilla Glue in addition to curing with the epoxy and HDI components of Belzona. Furthermore, the HDI and the isocyanates in Gorilla Glue polymerize together in the presence of moisture. These reactions allow the formation of co-polymers, rather than inter-penetrating polymer networks, of epoxy, isocyanate, and amine species.

3.3.2 Partially Methacrylated Epoxy With Gorilla Glue Gorilla glue was mixed in a 50/50 weight ratio with the PME material. The combination was found to cure to a very hard product and reduce the expansion and foaming associated with the Gorilla glue moisture curing reaction. The cure reaction was found to proceed with or without ambient moisture present. This resulted in two part adhesive moisture/moisture free curable hybrid epoxy.

3.4 Cure Rate Testing

3.4.1 Pan Mix Testing Adhesives were mixed in 5 g disposable plastic mixing pans to establish basic curing characteristics. Commercial adhesives were prepared as recommended by the manufacturers specifications. Once baseline curing rates and performance was established, commercial variants and modified adhesives were tested. Curing rates were categorized as useful pot life, cure to handle, and full cure. The resulting overall quality of the cured adhesive was also recorded. Approximately 10 g of each adhesive mixture was tested at $20\text{ }^{\circ}\text{C}$. Pot life

was considered over when the adhesive exhibited a reduced ability to wet a surface. Handling time was reached when the mixing paddle was firmly fixed in the adhesive. Full cure was established by indenting the adhesive with a medium ball point pen and determining how long it took to reach maximum hardness. This information was used for later experimental planning.

3.4.2 Exothermic Testing 15 g of each sample was mixed in a 50 mL polypropylene disposable beaker. Into the center of the adhesive mass, a K-type wire thermocouple was inserted. The temperature was recorded once a minute using an Omega Engineering (Stamford, CT) HH2002AL logging thermometer. In the case of very exothermic reactions, temperatures were recorded from the HH2002AL display by hand every 15 seconds. Readings were taken through the exothermic peak and sufficiently after to establish a cooling trend.

3.5 Lap Shear Samples

3.5.1 Specimens Lap Specimens were obtained which consisted of five connected test specimens cut from single piece of 1.6 mm thick aluminum sheeting. The specimens were cut 101.6mm long by 25.4 mm wide as indicated under ASTM D 3165-95 “Standard Test Method for Strength Properties of Adhesives in Shear by Tension Loading of Single-Lap-Joint Laminated Assemblies”. The specimens were fitted onto a pegged aluminum platform panel which provided 12.7 ± 0.3 mm overlap between prepared test surfaces.



Figure 3: Dry lap shear plate setup prior to placement of alignment cover panel.

3.5.2 Plate Preparation Specimen plates were abrasive blasted using 180 grit aluminum oxide powder. Blasting was sufficient to assure all surfaces used for adhesive contact were fully cleaned to remove any existing oxide layer. After blasting, specimen plates were triple rinsed with distilled water and allowed to air dry. Once dry, the blasted area was then treated with a 4.5 pH mixture of distilled water with 1 wt% GPS. GPS is a commercially used coupling agent shown to be effective in increasing the bond strength between epoxy adhesives and aluminum surfaces (20). The GPS was allowed to saturate the blasted aluminum surface for 3 minutes. The specimen plate was then tilted and excess GPS was allowed to run off. Once dry the plates

were heated at 200 °C for 60 minutes. Treated plates were used within 24 hours of being prepared.

3.5.3 Dry Application Methodology Once prepared, two lap specimen plates were placed on the pegged aluminum alignment panel. 20 g of adhesive were mixed on a 6 g mixing tray with a wooden paddle. Once mixed, a new paddle was used to apply the adhesive onto the designated 12.7 mm overlap areas. The corresponding prepared top panel was subsequently overlapped and pegged into place. Dummy plates were used to maintain proper spacing and release film was used to prevent adhesive from sticking to the alignment panels. The weight of the top alignment panel was sufficient to provide intimate contact between lap specimens and the adhesive applied. The panel pegged on top of the specimens being held by the base panel and provided a uniform bond line thickness (Figure 3).

3.5.4 Wet Application Methodology The same alignment equipment setup was used for the wet application methodology as dry. The aluminum alignment panels and specimen plates were kept under 7 cm of 21 °C tap water for 5 minutes prior to adhesive application. The top half of the lap specimen plates were removed from the water and were drip dried 3 seconds prior to adhesive application. Immediately after application the lap plate was placed back into the water and adhered to the submerged corresponding bottom specimen plate. The top alignment panel was applied and samples were cured underwater for 12 hours. Release fabric was used to prevent adhesion to alignment panels.

3.5.5 Instron Testing Lap plates were cut into individual lap specimens and marked accordingly. Samples were tested following ASTM designation D 3165-95. Spacers were used to assure the long axis of the specimens would be in direct alignment with the direction of applied force relative to the center of the grips. Load cells were selected according to ASTM recommendation to assure the maximum load fell between 15 and 85% of the load cell capacity. Cross head loading speed was set to 1.27 mm/min. Recorded information included failure load, bond line thickness, and shear area.

3.6 Thermal Enhancement

3.6.1 MRE Exothermic Testing Zesto Therm MRE heater packages were dismantled and the heating components removed. The material consisted of super corroding alloy comprised of Mg annealed with Fe, NaCl and inert filler (21). Mg acts as an anode and Fe the cathode. The addition of water to NaCl creates a sufficient electrolyte to allow free electron movement and subsequent corrosion of the Mg.



Figure 5: Generalized reaction of Mg/Fe alloy supercorrosion (21).

Since the Mg and Fe are annealed together, the reaction is extremely rapid. 15 g samples were mixed with 5 g of water in 50 mL polypropylene disposable beakers and temperatures logged with an Omega Engineering HH2002AL logging thermometer. Samples routinely reached 100

°C from an initial temperature 23 °C within 5 minutes. Temperatures would begin to decline after 2-3 minutes. The reaction was irreversible and single use in nature.

3.6.2 Augmentation of Epon 828 with Mg/Fe alloy The heating component portion of the MRE heater was removed and mechanically rendered into a coarse powder. The metal alloy fraction was separated from the NaCl and binder with a magnet. Once removed, the metal was pulverized into a powder less than 500 microns in size using a mortar and pestle. 15 grams of metallic augmented Epon 828 epoxy was prepared which contained 1.5 g powdered metal and 1.0 g NaCl. PACM amine was used as the curing agent.

3.6.3 Augmentation of Gorilla Glue Gorilla Glue was used as another base for testing the addition of Mg/Fe metal powder and NaCl. 15 grams of augmented Gorilla Glue was prepared which contained 1.5 g of powdered metal and 1.0 g of NaCl.

3.6.4 Augmented Samples Aqueous Reaction Curing temperature rates were determined for un-augmented samples of Epon 828/PACM and Gorilla Glue cured with and without water added. Augmented samples were then prepared and curing temperatures logged again with and without water added. This was done to differentiate the separate thermal effects of water addition, metals and salt addition, and combined metals salts and water addition. The goal of the testing was to determine if the combination of Mg/Fe, NaCl, and water would produce a sufficient exothermic reaction to increase cure rates.

Epon 828 was selected as it cured with PACM over several hours and has a very slow thermal increase during the first few hours. Any additional exothermic reaction would be distinguishable by a faster/higher temperature increase compared to the straight Epon 828/PACM cure.

Gorilla Glue was also selected after testing indicated Epon 828/PACM experienced a significant thermal reaction when mixed with water. The Gorilla Glue experienced a much lower increase in thermal reaction when water was added. This lower reaction rate with water provided easier delineation of increased thermal production from the Mg/Fe additive when mixed with water.

4. RESULTS AND DISCUSSION

4.1 Pot Life and Cure Time A wide variation in cure rates was encountered. For thin film thicknesses at ambient humidity, the CA40 adhesive made near instantaneous bonds. However, at any significant thickness, it cured only after extended periods of time. For rapid repair use, only the Belzona 1221 adhesives cured rapidly enough for serious consideration. The cure time of Belzona 1221 was decreased from minutes to seconds by the addition of Gorilla Glue to the solidifier component. It was found that 30 wt% added to the solidifier was the optimal amount. Though 70% wt% Gorilla Glue added to the Belzona 1221 solidifier was also tested, it was found during dry lap shear testing to have reduced adhesive strength and was not tested any further. Cure rate of PME/CoNap/Trigonox/PACM was found to be very dependant on CoNap and Trigonox. At 1.1 wt% CoNap and 1.6 wt% Trigonox, the adhesive's useful pot life was approximately 30 seconds. In contrast at 0.3% CoNap and 3.2 wt% Trigonox the useful pot life was near 30 minutes. Other adhesives cured fast enough for quick repair use.

Table 1: Adhesive cure test results to determine approximate cure rates and adhesive properties.

Adhesive Tested	Pot Life	Handle Time	Full Cure	Adhesive Property
Belzona 1221	3-4 minutes	15 minutes	75 minutes	Excellent Adhesive
MSUWG	20-30 minutes	1-2 hours	24 hours	Excellent Adhesive
A-788 Splash Zone	30-40 minutes	2-3 hours	24 hours	Excellent Patching Material, Poor Adhesive
Gorilla Glue	30-60 minutes	3-5 hours	24 hours	Excellent Adhesive On Moistened Surfaces
CA-40	0-24 hrs	0-24 hrs	1-24 hrs	Excellent Thin Bond, Poor Thick Bond
Epon 828/ PACM	4 hours	12 hours	24 hours	Fair Adhesive
Epon 828 + Gorilla Glue	> 2 weeks tested	N/A	N/A	None
50/50 PME/Gorilla Glue	30-60 minutes	3-5 hours	24 hours	Excellent Adhesive
PME/CoNap/Trigonox/PACM	30 minutes	2-3 hours	24 hours	Brittle when cured. Cure rate CoNap Trigonox dependant
Belzona 1221 Modified Solidifier- 30% GG	30-60 seconds	5 minutes	10-15 minutes	Extremely Fast Cure, Excellent Adhesive Excellent Patch Material
Belzona 1221 Modified Solidifier- 70% GG	30-60 seconds	5 minutes	10-15 minutes	Extremely Fast Cure, Excellent Adhesive Excellent Patch Material

4.2 Exothermic Testing Results Temperature logs were compared to known cure characteristics of the various adhesives. Thermal characteristics varied widely between adhesive classes. Trends in peak exothermic activity followed the trends in overall cure times. In other words as temperatures increased faster and higher, the cure rate of the adhesive increased and the

cure time decreased. The temperature logs were able to show how these formulated adhesive variations affected their cure rates relative to the baseline adhesives used.

The most significant increase in thermal rate for a modified adhesive was found in the Belzona 1221 modified solidifier group. Addition of Gorilla Glue to the Belzona solidifier significantly increased the thermal rate of curing as seen in figure 4.

Curing of the partially methacrylated Epon 828 resin was found to be extremely dependant on the concentrations added of Trigonox and CoNap. By altering the concentration of these components, the adhesive could be tailored to cure in seconds or hours. Exothermic testing was performed based on stoichiometric calculations for PACM and 0.5 wt% Trigonox and 0.005 wt% CoNap.

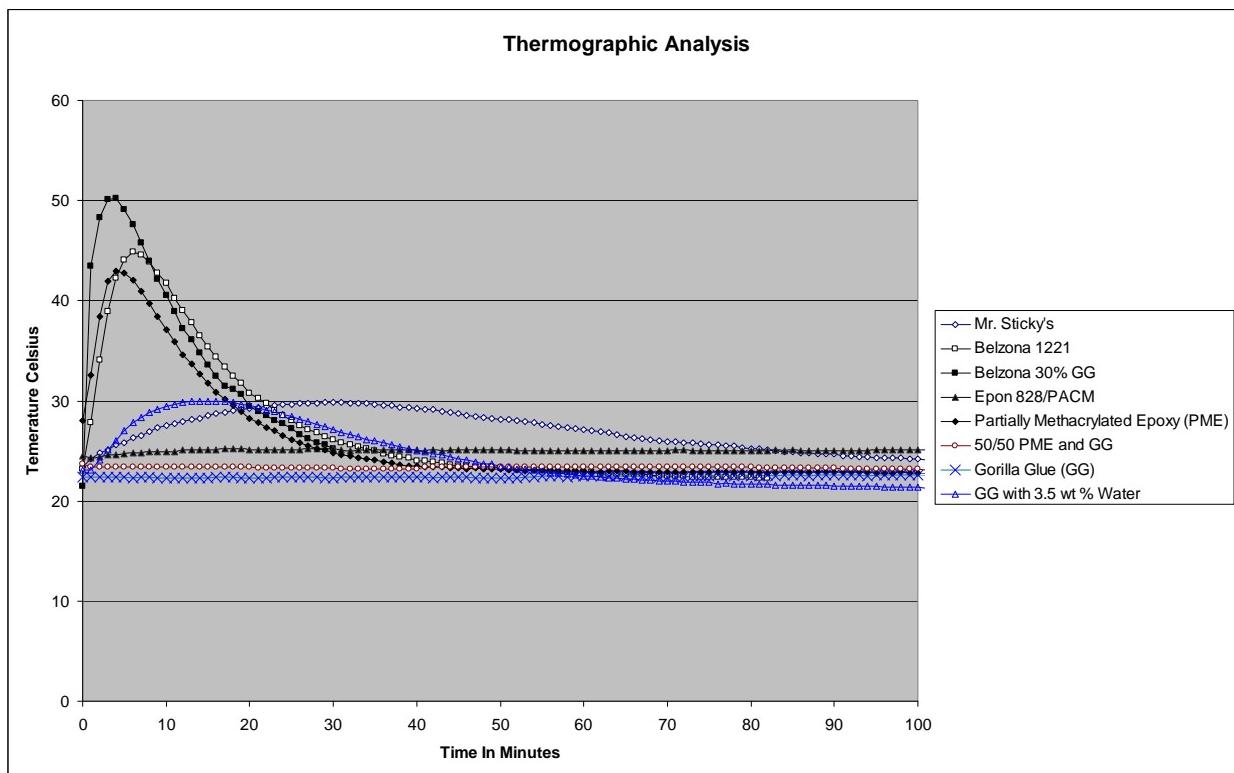


Figure 4: Thermographic analysis of adhesives.

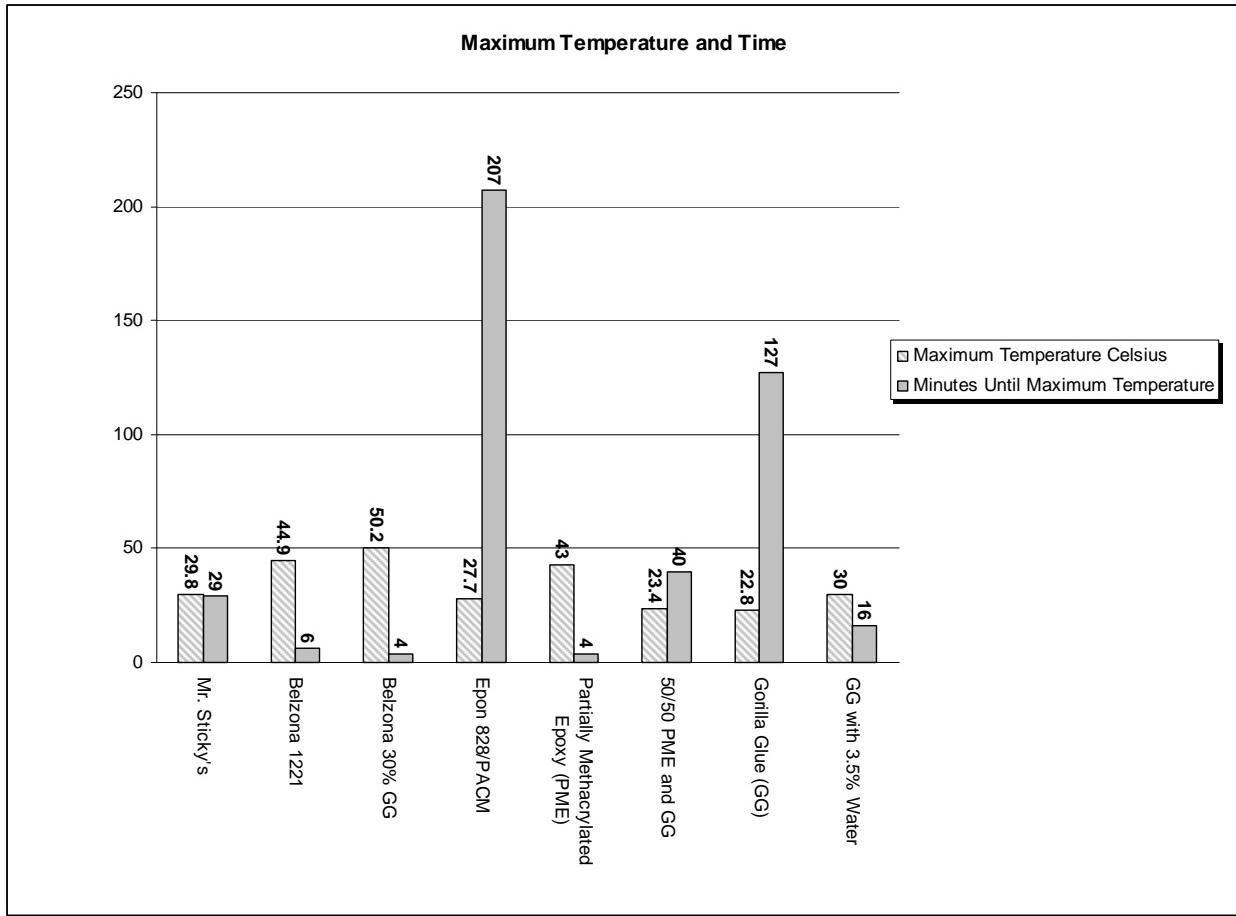


Figure 5: Maximum temperature reached and time to achieve it.

4.3 Lap Shear Results

4.3.1 Dry Lap Shear Results Lap shear strengths were measured and compared between the dry prepared commercially available and modified adhesives. The lap shear results for the commercial adhesives were similar to the manufacturer's claims (1, 8, 13, and 14). The Belzona 1221 modified solidifier with 30 % Gorilla Glue provided a factor of 2.5 increase in the dry bonding strength. This gave it the highest lap shear test average of 20.78 MPa. Dry lap shear results for the partially methacrylated Epon 828 and Epon 828/PACM were nearly identical (Figure 6).

4.3.2 Wet Lap Shear Results Testing of wet prepared lap shear samples yielded data not provided by the manufacturer. In every instance, wet lap shear strengths were lower than their corresponding dry lap shear counterparts. Belzona with 30% Gorilla Glue added to its solidifier showed significant wet adhesion improvement. Gorilla Glue provided the highest level of wet adhesive strength tested. Though water exposed Gorilla Glue foamed significantly, the interior bond portion remained relatively unaffected. Wet cured 50/50 PME and Gorilla Glue formed an extremely weak bond. When cured underwater, partially methacrylated Epon 828 resin did not show signs of reaction (whitening) as did Epon 828/PACM. Wet lap shear results for the

partially methacrylated Epon 828 were higher than the Epon 828/PACM. Cyanoacrylate adhesives reacted rapidly when in contact with water, thus wet lap plates could not be prepared and lap strength of zero was assigned (Figure 6).

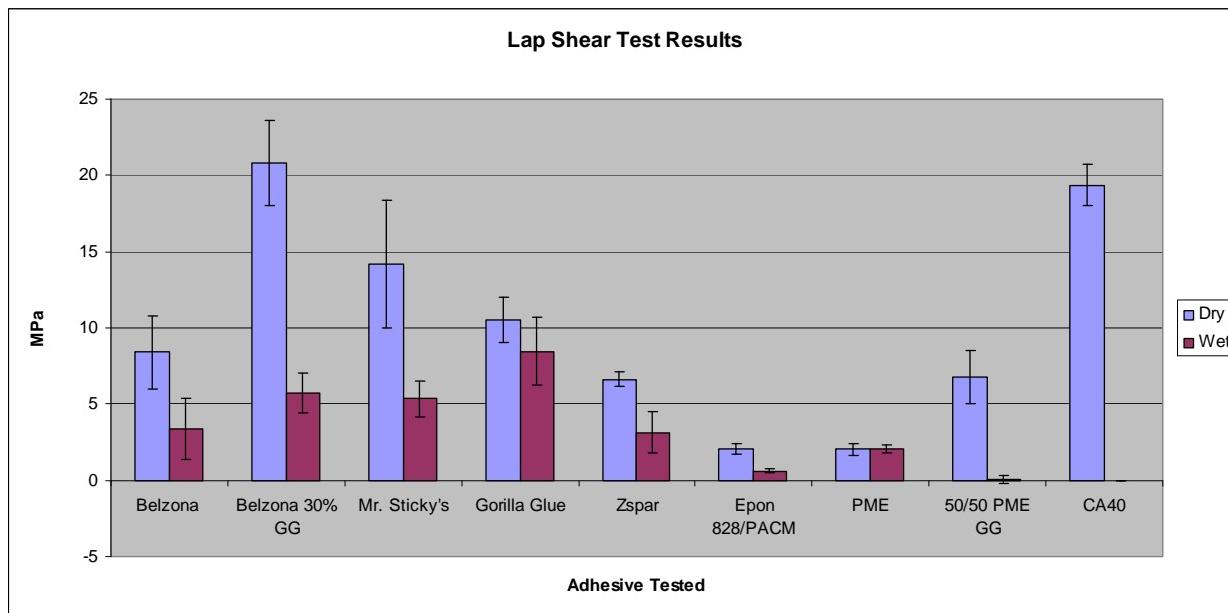


Figure 6: Lap shear results showing dry and wet results for commercial and modified adhesives.

4.4 Thermal Enhancement Results

4.4.1 Epon 828 Epon 828/PACM with added water reached a thermal peak of 99 °C while with the metal augmentation and water only reached 35.2 °C. Metal augmentation of Epon 828/PACM without water produced even lower thermal cure rates than the Epon 828/PACM. As seen in figure 7, results indicated that the metal augmentation decreased the thermal activity of the Epon 828/PACM cure with and without water added.

Production of gaseous byproduct could be seen in all augmented Epon samples with and without the addition of water. The gas production was significantly greater in the water added sample. Mechanisms responsible for the reduction in thermal activity will be further investigated.

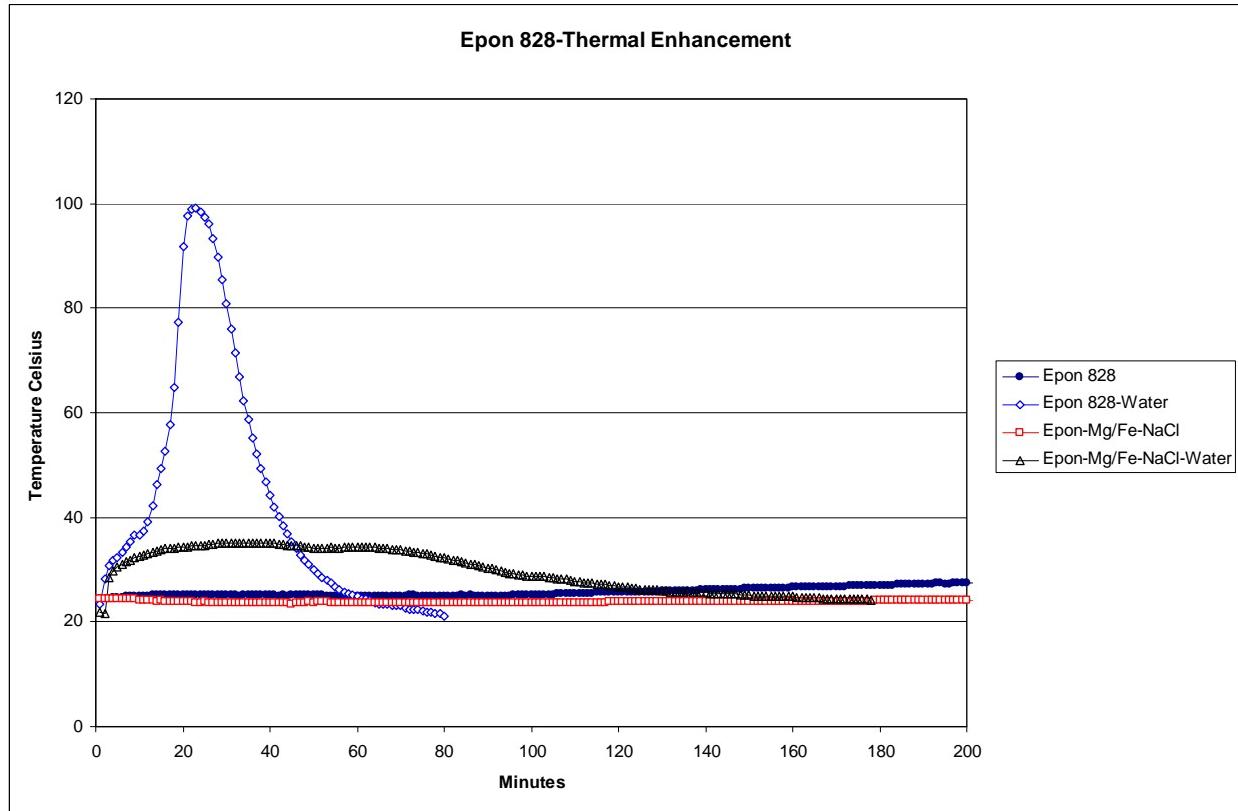


Figure 7: Thermal enhancement of Epon 828 cured with PACM.

4.4.2 Gorilla Glue In contrast to the Epon 828 epoxy, the addition of Mg/Fe and NaCl increased the exothermic maximum over both the air dried Gorilla Glue and Gorilla Glue with water added. The Gorilla Glue with water added experienced a temperature peak of 30 °C while the metal augmented water version peaked at 33 °C. No gas production surrounding the metal particles was seen in any of Gorilla Glue samples.

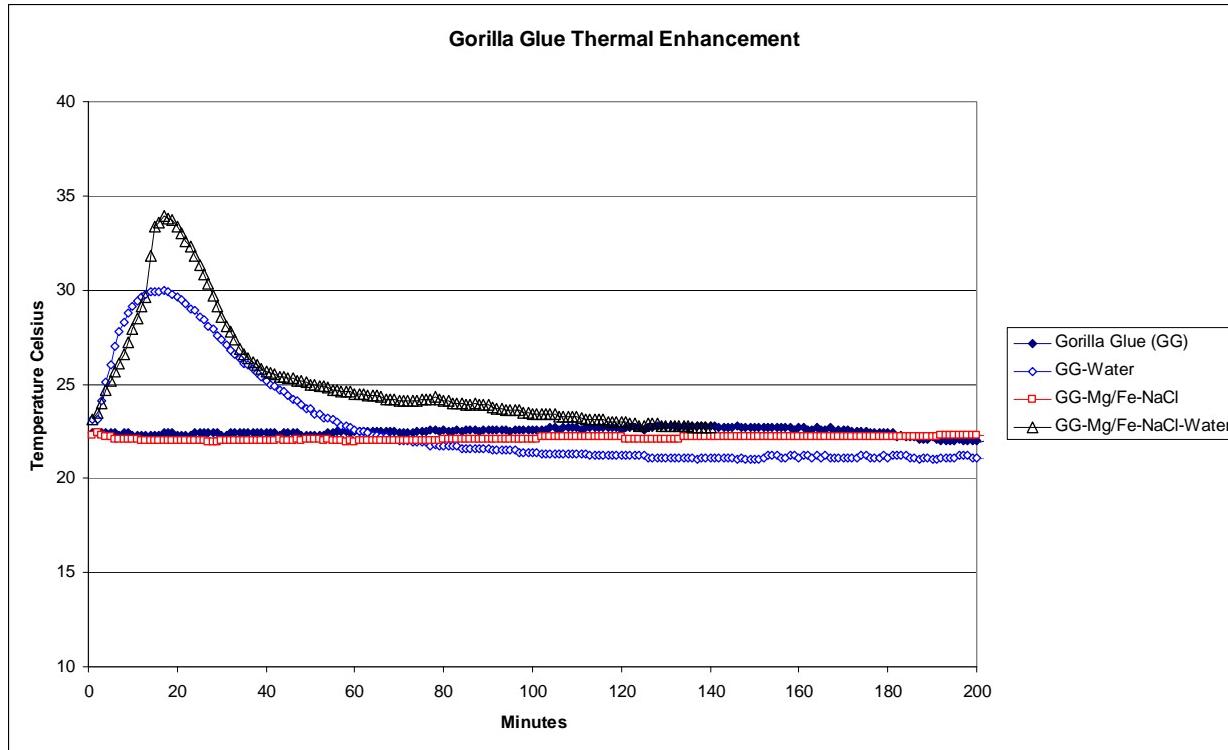


Figure 8: Thermal enhancement of Gorilla Glue.

5. CONCLUSION

Modification of existing commercial epoxies yielded increased dry and wet lap shear strengths and decreased cure times. This was primarily observed in the Belzona 1221 modified solidifier with 30 % Gorilla Glue adhesive. The modified Belzona 1221 had the highest overall single (20.78 MPa) dry lap shear results and reached full dry cure in 10-15 minutes. It also had a marked increase in wet lap shear strength. Other novel approaches yielded partially methacrylated epoxy hybrids that show promise in their ability to cure underwater without significant water reactions. Gorilla Glue out performed the two part epoxy systems during wet lap shear testing. Therefore, a means to increase the cure rate of Gorilla Glue will be investigated.

Thermal logging of cure reactions proved useful to determine the effects of modification to adhesives. This also provided information on how interactions with water affected the cure rates of adhesives. This method will soon be used to evaluate the cure rate of these adhesives in wet environments.

Efforts to increase cure rate by introduction of super corroding metals and salt to adhesives had mixed results. The incorporation of augmentation materials into adhesives did provide some increase in peak cure temperature in the water curing Gorilla Glue but only marginally. Corrosion of incorporated metals was observable in the Epon epoxy testing samples but reduced the thermal peak. Further research into reaction mechanism is required. The amount of water

needed to provide sufficient electrolyte activity to the Mg/Fe components caused significant degradation to the overall properties of the adhesives. In addition, the effect of these additives on adhesion strength must be further measured.

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